ALLIANT TECHSYSTEMS

Flexible Manufacturing, Rapid Prototyping of Solid Polymer Electrolyte (SPE), Rechargeable Ambient Temperature Batteries: Part A and Part B

1st Quarterly Report for period 8/94 to 10/94

February 24, 1995

Hsiu-Ping Lin
Alliant Techsystems Inc.

Denis Fauteux
Arthur D. Little, Inc.

Office of Naval Research
Ballston Tower One
800 North Quincy Street
Arlington, VA 22217-5660

Contract No: N00014-94-C-0163

CHAPTER 1.0

INTRODUCTION

The overall objective of this program is to develop flexible manufacturing process capable of adapting various polymer electrolyte and electrode combinations and cell configurations for SPE-based lithium batteries . The program is structured into two parts: Part A: Development of flexible manufacturing for rechargeable polymer batteries; and Part B: Exploratory R&D on the rechargeable polymer technology. This two-year development effort begins with the establishment of the SPE process techniques using Alliant Techsystems' (ATK) polymer battery technology. Our baseline technology is as follows:

Cathode:	$LiCoO_2$
Positive Current Collector:	stainless steel
Anode:	Li
Negative Current Collector:	nickel
Electrolyte	$LiAsF_6$/polyacrylonitrile (PAN)-based polymer electrolyte

Our PAN-based polymer electrolytes offer excellent ionic conductivity , 1.5×10^{-3} to 4×10^{-3} S/cm, in the temperature range of -20°C to 100°C. The electrochemical stability of this thin film has demonstrated a broad potential window of 2.3 V to 4.3 V, suitable for the use of the Li/Li_xCoO_2 couple. Laboratory cells based on this chemistry have demonstrated a 200 cycle life at a 80 to 90 percent DOD.

Polymer batteries contain thin electrodes and electrolyte films to provide a sufficiently large surface area to sustain substantial rates for practical applications. The quantity of components needed for each battery is enormous due to the use of thin parts. The ability to produce consistent and homogenous films is therefore crucial to this technology for manufacturing purposes. Automatic coating is required to provide uniform large quantity films. In Part A of the program, we will collaborate with Arthur D. Little, Inc. (ADL) in process development and production of flexible polymer electrolyte composite cathode laminates. Both ATK and ADL have the same type of pilot coaters to ensure control of the process development and technology transfer. This initial effort will be focused on improving the baseline processing to enhance energy density. A battery assembly line will be designed, fabricated and installed for manufacturing batteries. A complete battery package including the battery case and charge electronic control will be developed in this part of the program.

The Part B of the program is a R&D effort. Its purpose is to investigate new candidates for the polymer electrolyte and anode. The solvent-free polymer electrolytes will be explored and compared to the current PAN-based electrolyte. A rocking chair system based on the carbon anode and $LiCoO_2$ cathode will be investigated. If successfully developed, these new candidates can be integrated into Part A of the program for manufacturing.

At the end of two years, we will demonstrate flexible manufacturing of SPE cathode films and two prototype flat-pack batteries for Thermal Weapon Sight (TWS) and notebook computer applications.

CHAPTER 2.0

DEVELOPMENT OF FLEXIBLE MANUFACTURING RECHARGEABLE POLYMER BATTERIES

2.1 Program Plan

A two-year program schedule and milestone is shown in Figure 2-1. The task of composite cathode film will be conducted by ADL. The technology developed by ADL will be transferred to ATK. Therefore, we can reproduce the process and evaluate the material in the cell level. In this twelve-month development effort, the cathode formulation will be optimized to achieve high energy density. The cathode manufacture process will be focused in the development of aluminum-based current collector for enhanced rate capability and as well as energy density. The second year effort will be on the setup of the production line for manufacturing the polymer batteries which include the cathode, anode and electrolyte components.

Another development effort is the prototyping of two model batteries for Thermal Weapon Sight (TWS) and notebook computer applications. This also includes the development of a "Smart" charger system.

2.2 ATK Polymer Technology Update

Prior to the contract award, ATK installed a pilot coater fabricated by ADL. This coater is designed to coat the cathode film on the current collector and then apply the electrolyte film on the cathode surface. Our internal IR&D funding has supported the process improvement using the coater since then. Figure 2-2 shows the early process technology using hand-drawing technique. The major issue was the high cell impedance which resulted in the cell testing conducted under applied pressure. The coater on the cathode coating section is now running consistently after intensive dry run. We scaled up the mixing quantity in order to use coater for cathode coating. Figure 2-3 illustrates the current process technology. The significant improvement on the interfacial bonding between the cathode film and the stainless substrate was attributed to the drying process. The dried cathode has good adhesion. Therefore, the cell testing can be conducted with free-standing cells without any external pressure.

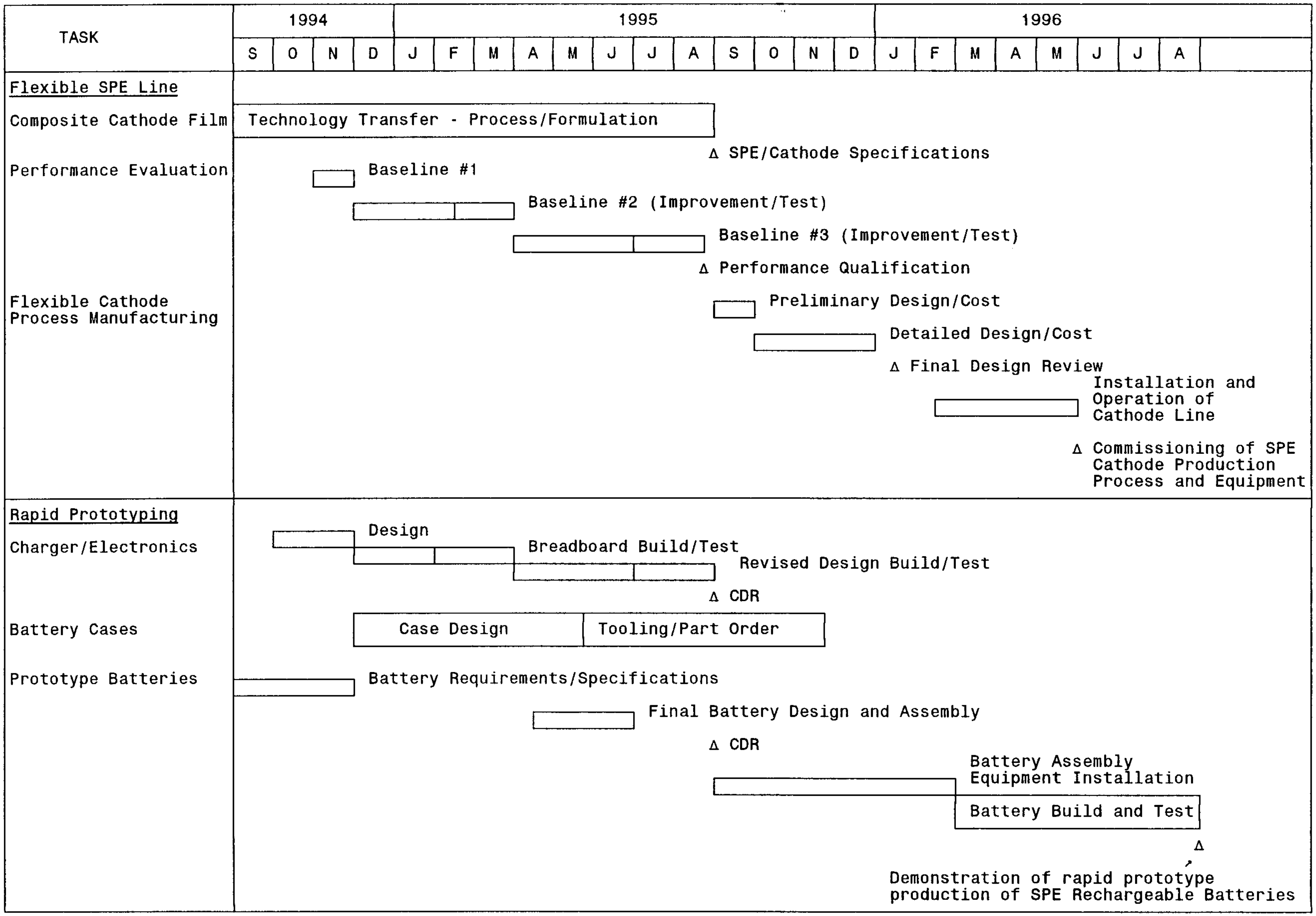
The drying process significantly improved the adhesion for the stainless steel substrate but not the aluminum substrate. Due to the high charging voltage required for the cell, the use of the aluminum substrate for current collector is necessary for the long cycle life. ADL is now developing a surface treatment for the aluminum current collector.

2.3 Flexible SPE Line

2.3.1 Advanced Aluminum-based Cathode Current Collector

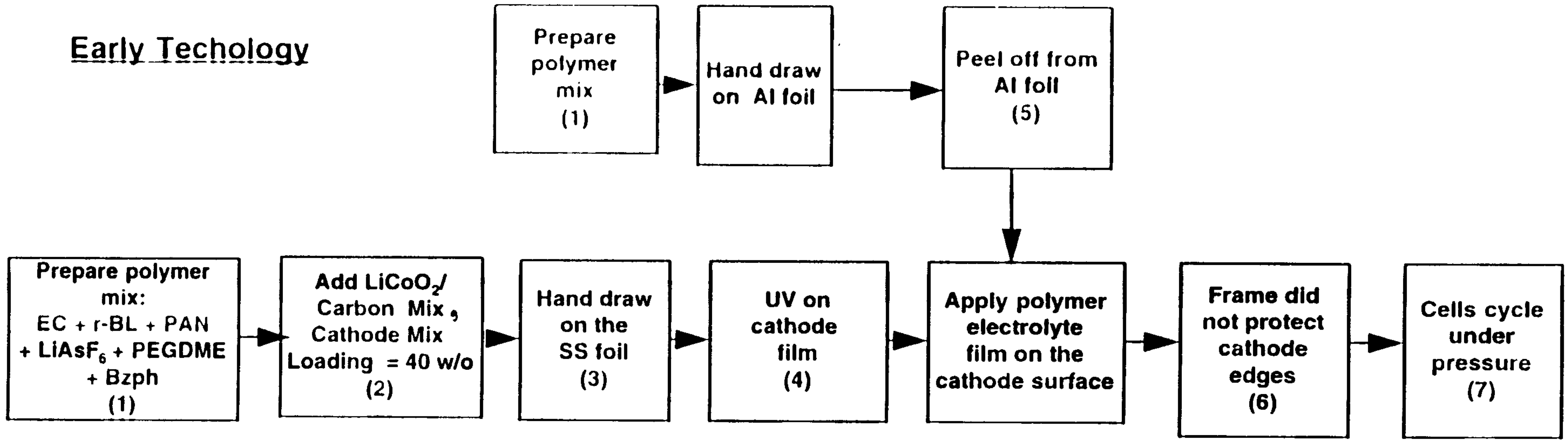
During this first reporting period, a detailed program plan has been prepared. This plan was presented during the program kick-off meeting on October 5, 1994. Due to the progress on the stainless steel substrate at ATK under internal funding, it was decided that the development of a composite cathode using an aluminum current collector should be prioritized

Figure 2-1. Flexible Manufacturing and Prototyping of SPE Batteries
Part A — Basic Tasks and Schedule



[S4773-1Q.wp]*paw

Early Techology



Issues:

(1) **Difficult to obtain the homogeneous polymer mix when PEGDME is added after PAN.**

(2) Low cathode loading (dictated by manual drawing) yielded low cell capacity.

(3) Uneven coating.

(4) Poor interface **bonding between cathode film and SS foil.**

(5) Difficult to peel off from Al foil. Stretched film results in **uneven thickness and pin holes.**

(6) Low cell yield rate due to shorting problem.

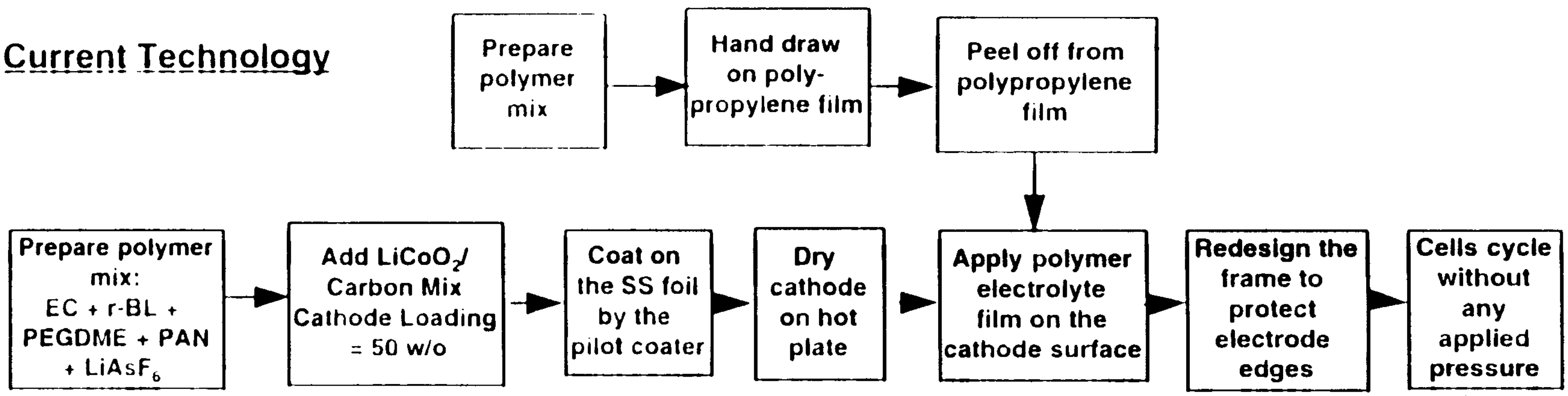
(7) **Applied pressure is needed in order to cycle cells.**

[E41208-3.ppt]*paw

Figure 2-2. Early Polymer Process

[S4773-1Q.wp]*paw

Current Technology



Remaining Issues:

(1) **Interfacial bonding between cathode and current collector substrate.**

(2) **Need to use aluminum current collector for cathode.**

[E41208-3.ppt]*paw

Figure 2-3. Current Polymer Process at ATK

[S4773-1Q.wp]*paw

in this program. The technical work performed during this reporting period was mainly focused on developing a surface treatment for an aluminum current collector

The main objective of this development effort is the continuous production of a thin (25 μm) aluminum foil current collector having an improved surface conductivity and an enhanced adhesion to the PAN-based gel electrolyte $LiCoO_2$-based composite cathode.

ADL has developed a patented surface treatment chemistry and a process to apply this treatment to thin foil aluminum cathode current collector substrates. This treatment has proven to increase foil's surface conductivity and improve adhesion of thermal-cured polymer electrolyte-composite cathode systems to aluminum based current collector substrates. ADL's surface treatment has been developed initially for use with $LiMn_2O_4$ based thermal cured composite cathodes. Consequently, the work performed during this period address the following issues:

- The effect caused by changes in the composite cathode formulation (i.e. thermoset versus thermal cured electrolytes and $LiCoO_2$ versus $LiMn_2O_4$ cathode materials).

- The effect caused by "large" scale processing of the aluminum foil (i.e. a sufficient linear feet of treated foil to run on the coater).

ADL has produced a number of treated aluminum foil current collector samples (of small size) two of which have been delivered to ATK for evaluation. These two samples were 27617-9a and -9b and were prepared as follows:

Sample 27617-9a: A preformulated graphite based primer, containing very small size graphite particles, a polymeric binder, and small quantities of surfactant and suspension stabilizer, was diluted with hexane in a primer to hexane ratio of 4:10. This primer suspension has approximate rheological properties for subsequent processing.

This primer suspension was gravity fed at a constant rate to a dispenser nozzle located before a #8 Mayer rod leaving a wet coating of < 5 μm thick. The hexane and mineral spirits were evaporated to dryness through a hot air convention stage. The coated aluminum foil was rewound on a stainless steel core and heat treated at 300°C for 12 hours in an air convection oven. The adhesion and appearance of the graphite primer was good and compared well to previous coating. However, the coated aluminum foil had some "wrinkles" which were not been observed when a 10 μm thick aluminum foil was used as a substrate. Five 20 cm x 10 cm samples were taken, four of them were sent to ATK, and one was retained by ADL for further characterization.

Sample 27617-9b: This sample was prepared using the sample 27617-9a coated aluminum foil to which an additional treatment step was performed. The additional step involved the coating of a water based solution of lithium manganese oxide precursor materials, suing a #8 Mayer rod. followed by a 5 minute heat treatment at 300°C of the air dried sample. Four samples were prepared, three were sent to ATK, and one was retained by ADL for further characterization.

The thermal profile which occurred during the processing of sample 27617-9a is illustrated in Figure 2-4. This figure represents a thermal gravimetric analysis of the simulated behavior of the primer suspension during heat treatment sequences. The initial step represents the evaporation, to dryness of only the mineral spirits diluents (no hexane) at the end of which 76% of the original weight is lost. The second conversion step occurs at 300°C. At the end of this step, approximately 85% of the graphite constituent is in the primer formulation. These results confirmed that the selected heat treatment conditions, for the preparation of the primed aluminum, are appropriate.

AC impedance spectroscopy was used to measure the resistivity of the treated aluminum current collector samples. Two-electrode symmetrical cell configurations were used for the measurements. The electrolyte was propylene carbonate (PC)-based gel system. The specific cell surface is 20 cm^2. Under these conditions, the treated aluminum current collector's (sample 27617-9a) resistivity was approximately 15Ω at ambient temperature (Figure 2-5). AC impedance measurements made under similar conditions yield a resistivity of 7.6Ω for sample 27617-9b.

Figure 2-6 summarizes the observed evolution of the treated aluminum current collector's (sample 27617-9a) resistivity as a function of storage time at ambient temperature. The mechanism responsible for the observed increase of the resistivity has not been identified. Although this trend has been observed for numerous samples, some samples have shown a more stable resistivity value as function of storage time.

The evaluation results will be reported in Section 2.3.2. ADL will produce a sufficient linear feet sample for pilot coater run during next reporting period.

2.3.2 Performance Evaluation

Two samples, 26917-9a and -9b, were received from ADL for evaluation. These two samples were graphite-treated aluminum substrate. The samples were dried in the vacuum oven at 100°C for 16 hours prior to use. Samples were initially coated with composite cathode mix using the doctor blade manually. The cells were then built without any further treatment on the cathode film. Five cells were built and none of the cell could support C/40 charging rate even with applied external pressure. It indicated that the cell suffered very high internal impedance and the graphite-treated surface did not improve the interfacial bonding. Another try was then conducted using the coater to apply the cathode film on the treated aluminum surface. The cathode film was then dried at 50 to 60°C for 3.5 hours. Significant adhesion between the cathode film and the substrate was obtained as the one observed in the stainless steel substrate. Cells built with this heat-treated cathode performed excellent. The delivered capacity compared to the stainless steel substrate is shown in Figure 2-7. A total of 16 cycles was obtained with > 95% efficiency to date.

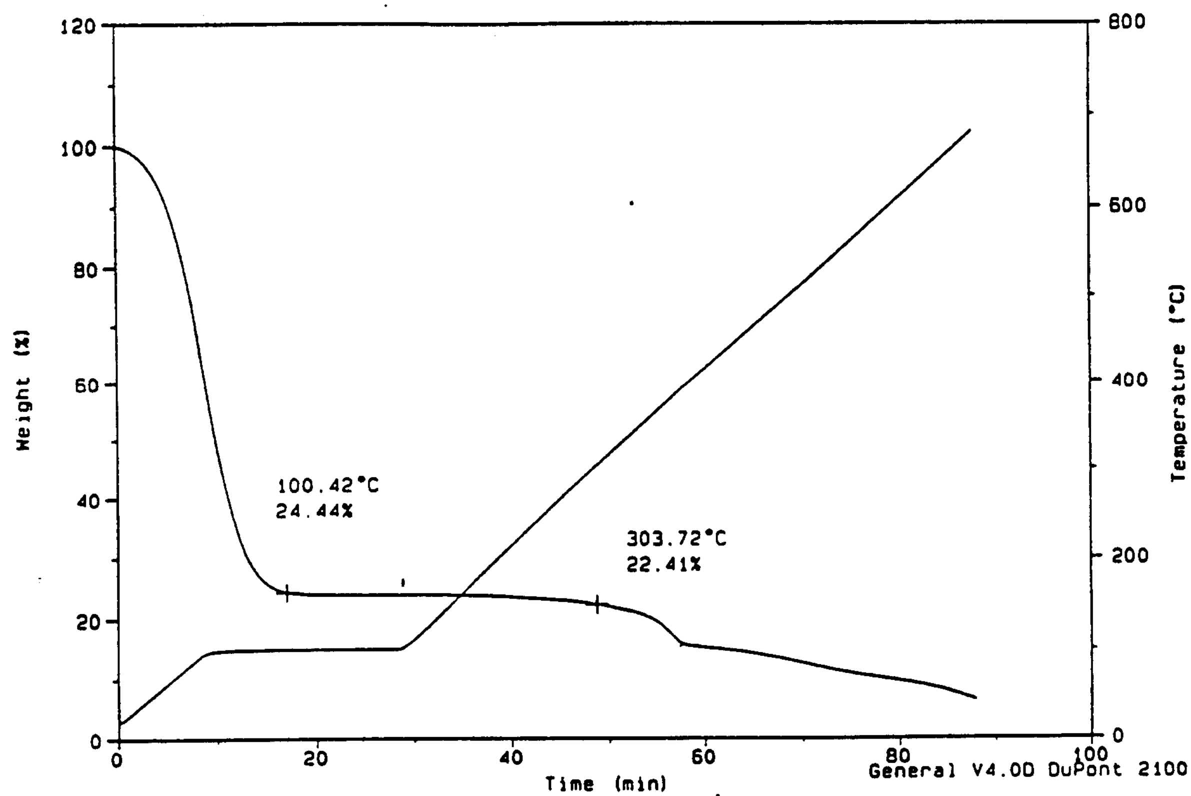


Figure 2-4. TGA Analysis of the Graphite Based Primer Formulation

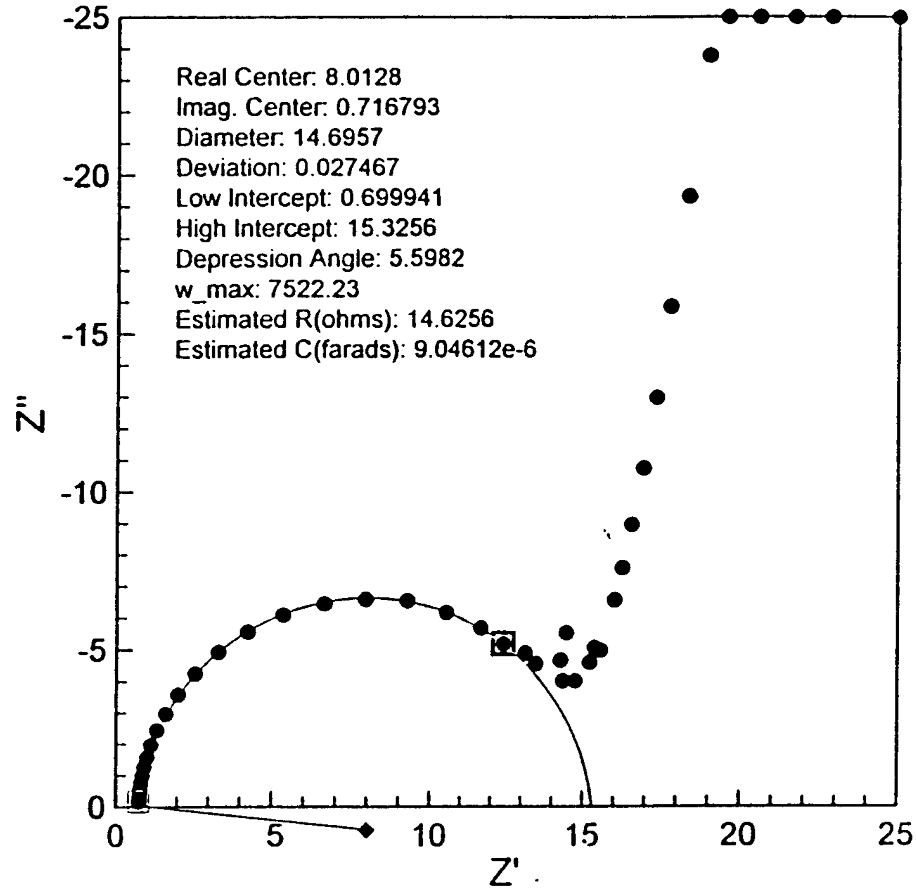


Figure 2-5. AC Impedance Spectroscopy Plot for Sample 27617-9a

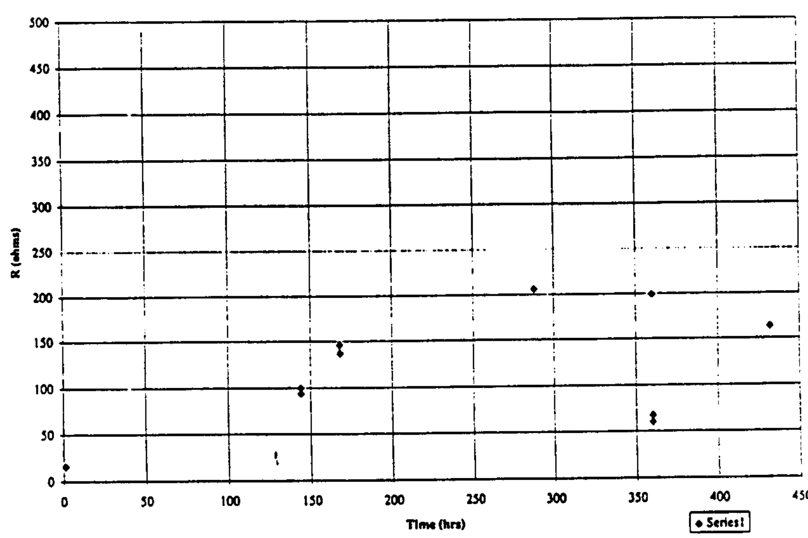


Figure 2-6. Evolution of the Surface Resistivity as Function of Aging Time for Sample 27617-9a

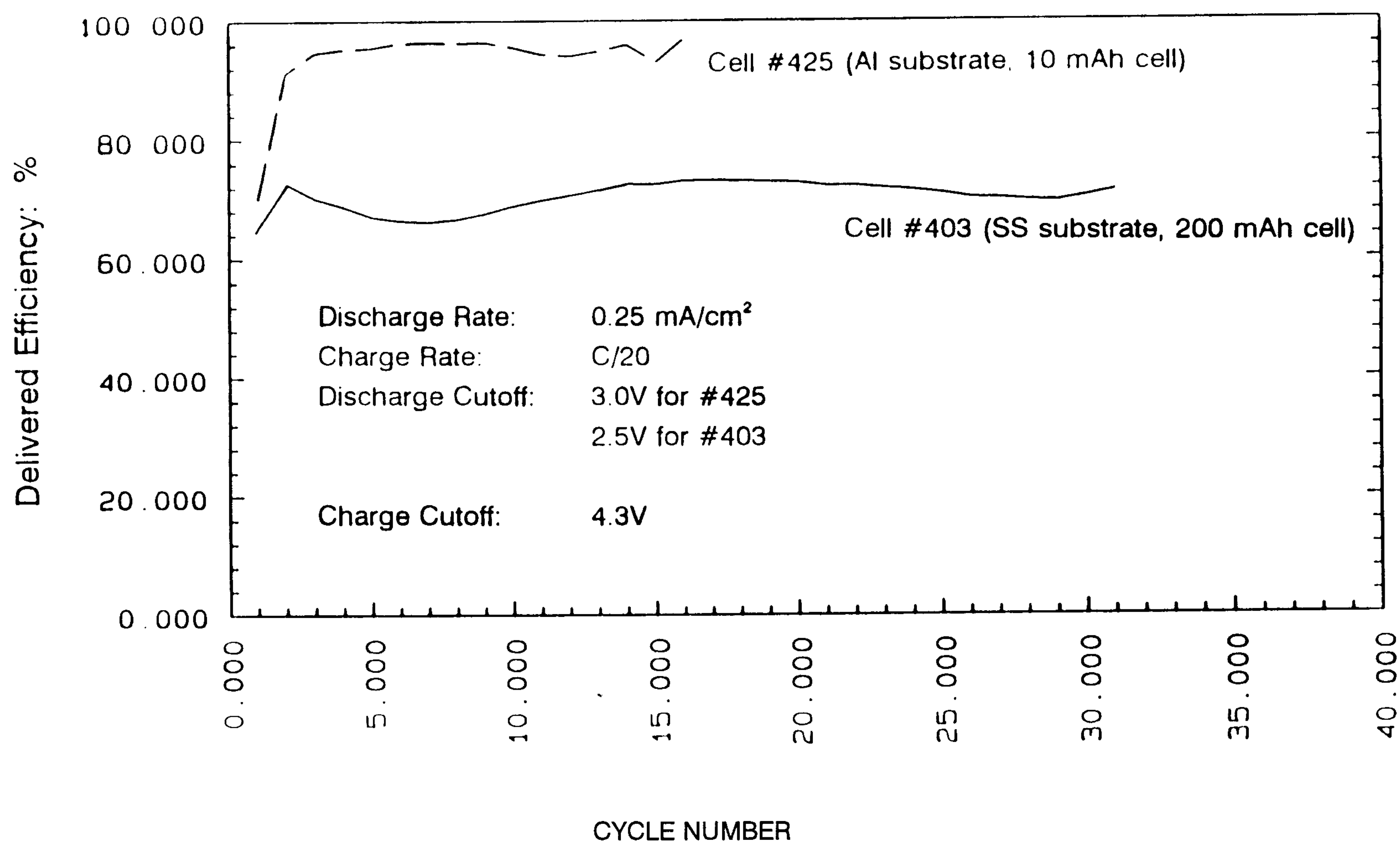


Figure 2-7. Polymer Cell Performance: Primed Al Substrate versus SS Substrate as the Positive Current Collector

[S4773-1Q.wp]*paw

2.3.3 Composite Cathode Evaluation

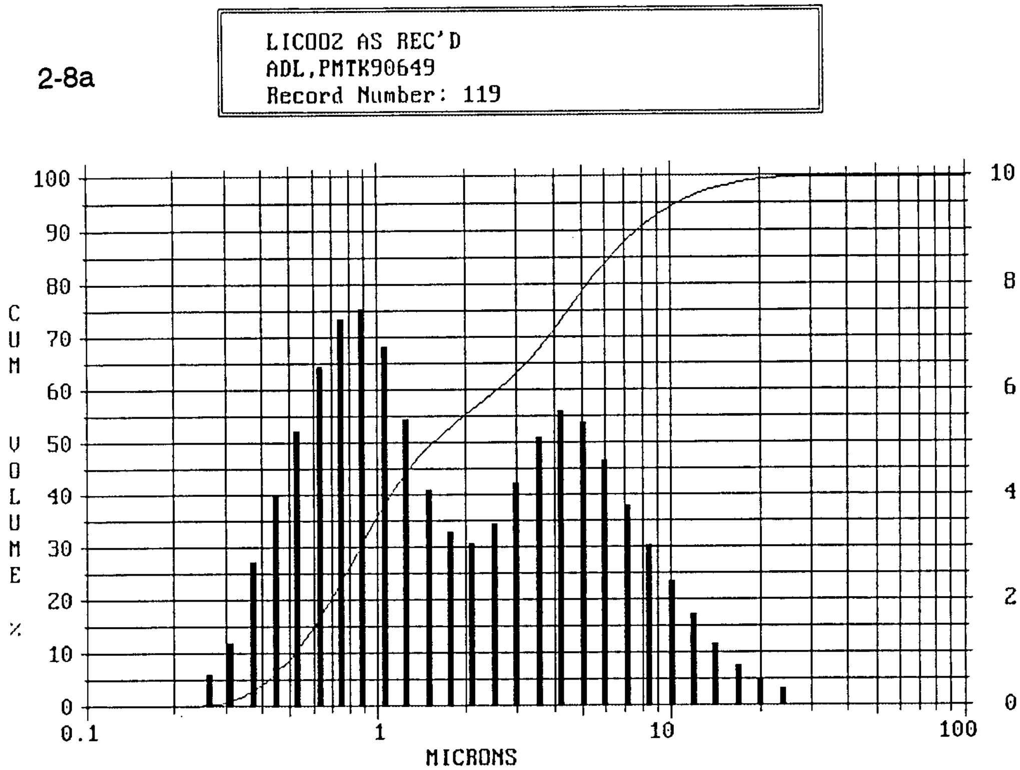
During this reporting period, ADL evaluated the effect of processing conditions on the $LiCoO_2$ and carbon particles size distribution. The particle size and particles size distribution are critical parameters to be controlled in order to achieve maximum composite cathode capacity and utilization.

The results of ADL's evaluation on ATK $LiCoO_2$ and carbon powders at different processing stages are summarized in Figure 2-8. As illustrated in Figure 2-8a, the particle size distribution of the $LiCoO_2$ is broad, ranging from 0.6 μm to 60 μm, having its mean cumulative volume at approximately 6 μm. The particle size distribution of the Vulcan-XC 72R carbon (Figure 2-8b) is narrower, as compared to the $LiCoO_2$, ranging from 0.3 μm to 5 μm and centered at 1.2 μm. After densification of the two powders together (mulling process), a bimodal particle size distribution is observed (Figure 2-8c). This particle size distribution pattern indicated that the mulling process does not impact significantly the particle size of each of the powders, and that each of the $LiCoO_2$ and carbon powders are relatively well separated from the other. This pattern is observed for all other powder samples provided. Figure 2-8d describes the particle size distribution of a sample sent to ADL by ATK for ADL use. This sample is very similar to the one described in Figure 2-8c, even if the bimodal distribution is slightly different. However, more importantly is the 10% volume fraction of the sample composed of particles larger then 10 μm. It is anticipated that these large particles will affect the uniformity and compactness of composite cathodes fabricated using this powder. Attempts have been made to further reduce the mean particle size and narrow the particle size distribution. Figures 2-8e and 2-8f illustrate the particle size distribution of $LiCoO_2$-carbon powder mixes after mulling and one grinding (Figure 2-8e) and two grindings (Figure 2-8f). The principle conclusions resulting from these particle size distribution analyses are:

(1) the first grind has no real effect on the particle size and particle size distribution of the powders, and

(2) the second grind appears to favor reaglomeration of the particles and produce a significant fraction (15%) of particles larger than 10 μm.

2-8a



2-8b

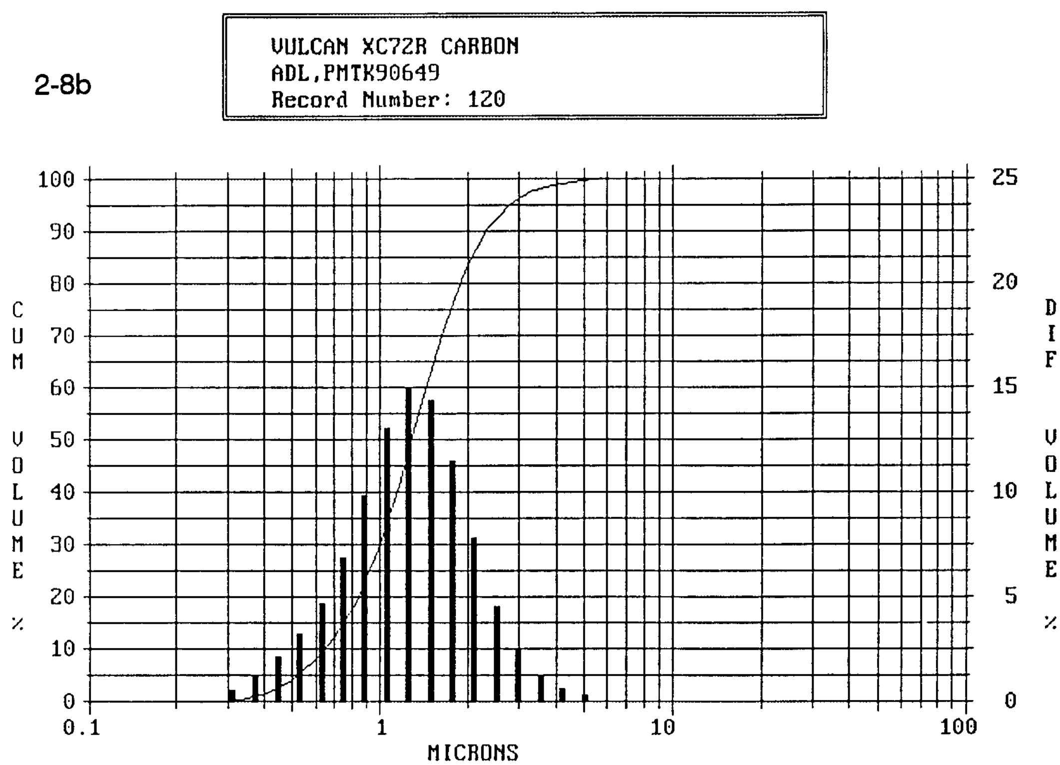
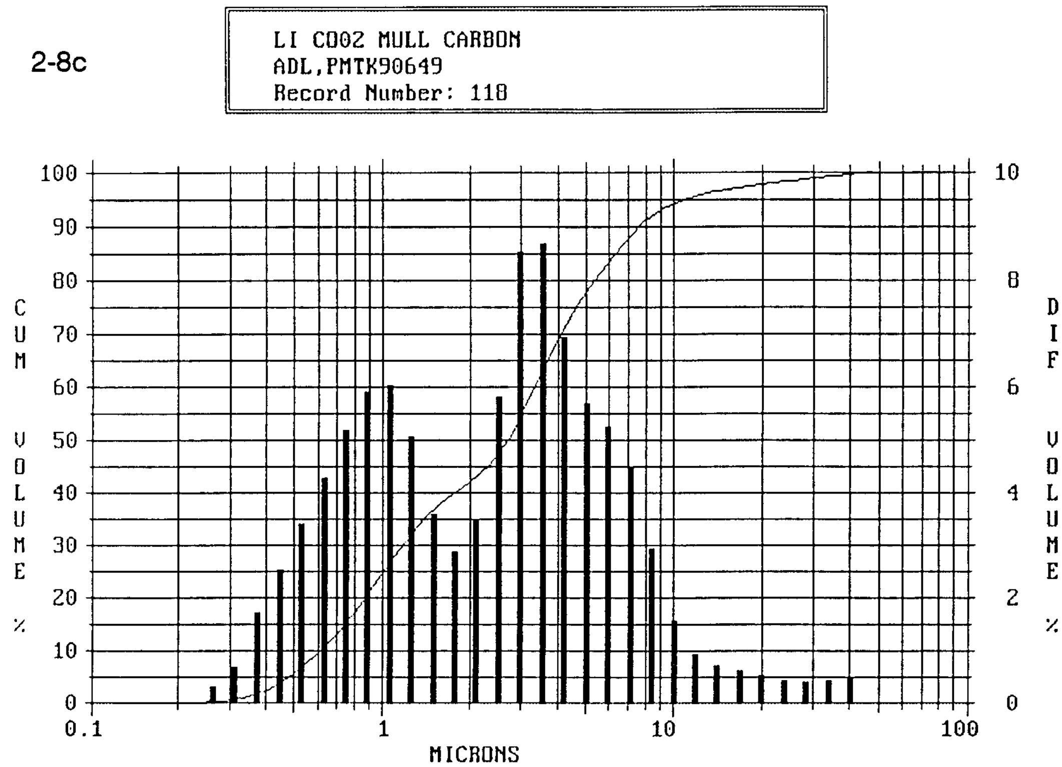


Figure 2-8. Particle Size Histograms for $LiCoO_2$ and Graphite Powders and Mixes

2-8c



2-8d

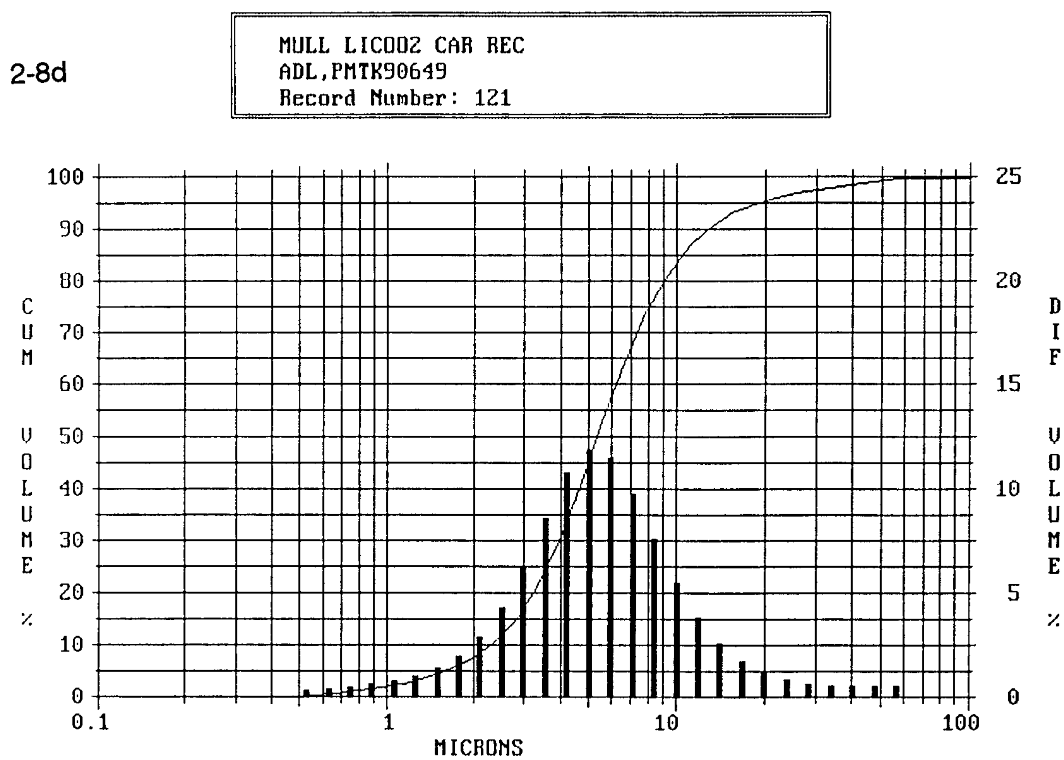
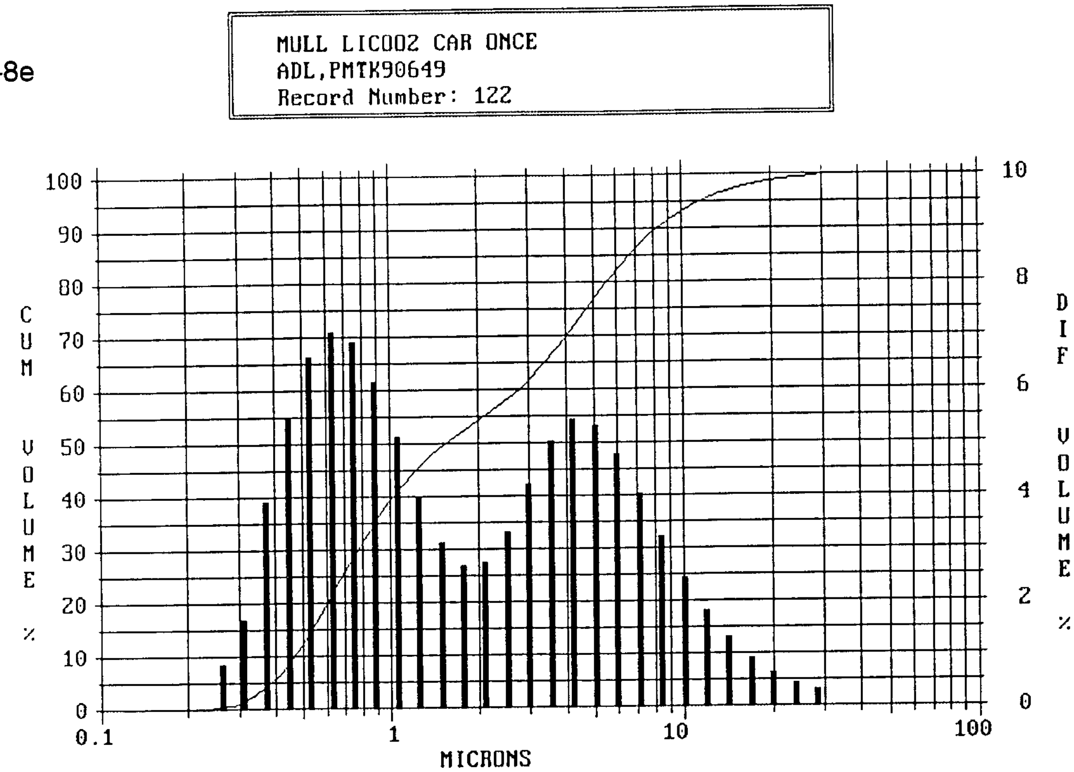


Figure 2-8. Particle Size Histograms for $LiCoO_2$ and Graphite Powders and Mixes

2-8e



2-8f

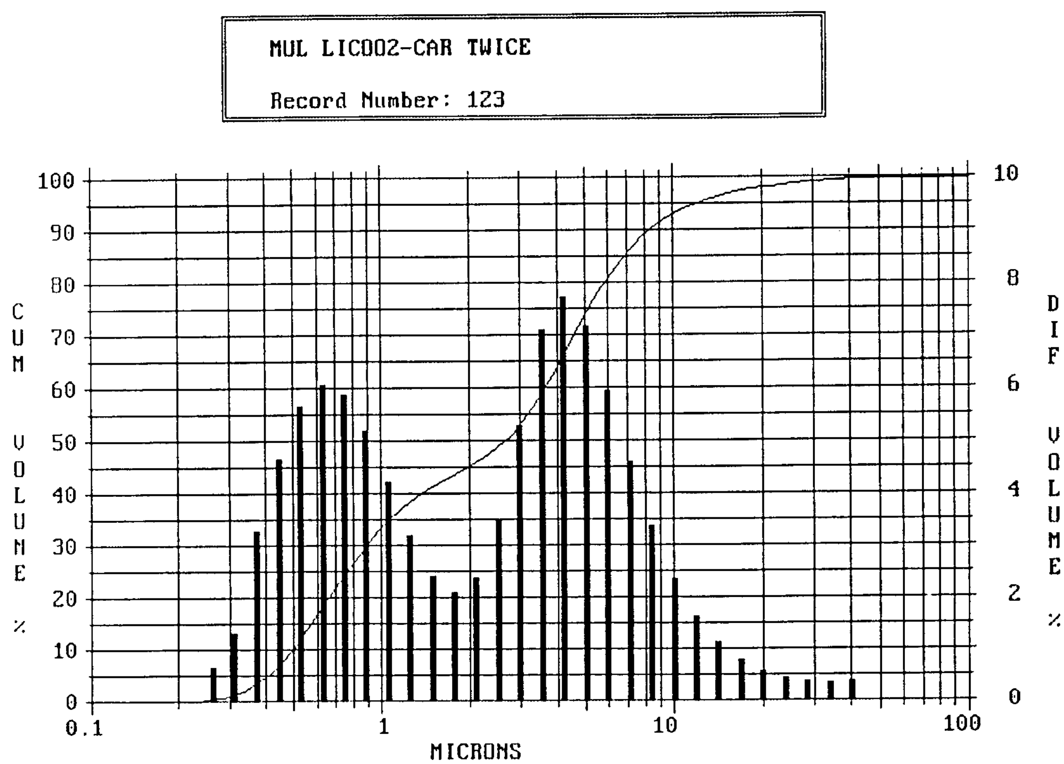


Figure 2-8. Particle Size Histograms for $LiCoO_2$ and Graphite Powders and Mixes

2-8g

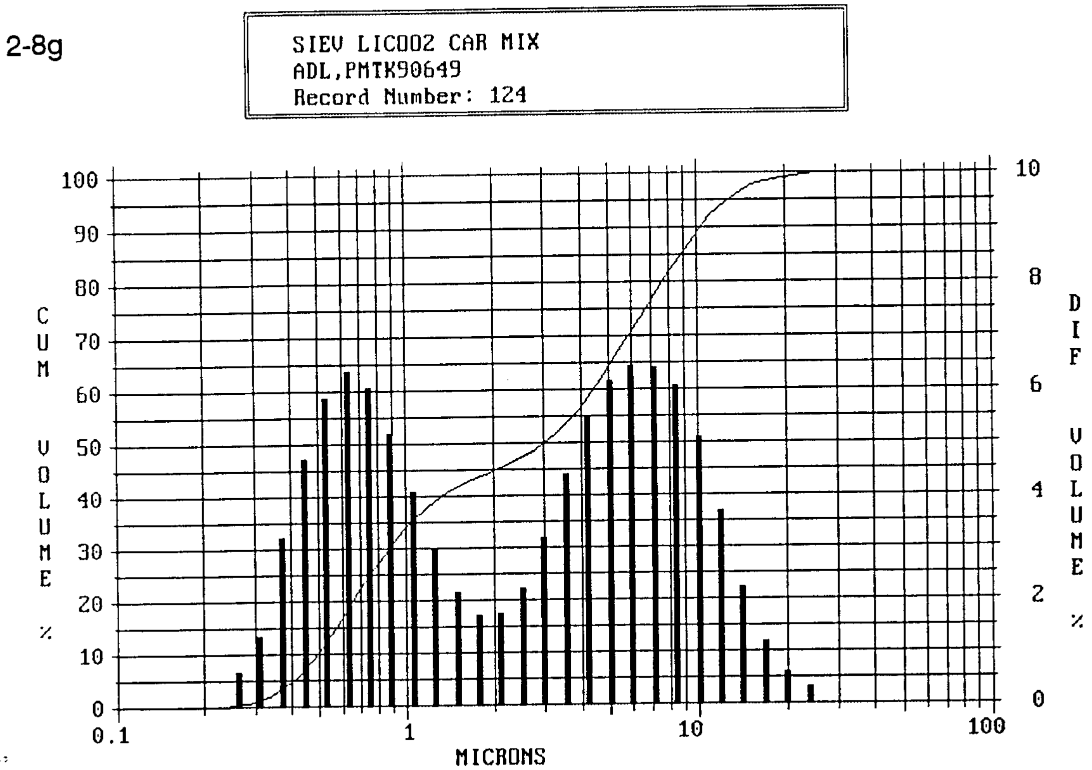


Figure 2-8. Particle Size Histograms for $LiCoO_2$ and Graphite Powders and Mixes

In Figure 2-8g, the particle size distribution of the mulled powders, sieved (-45 μm), grounded and resieved (-20 μm) is presented. Considering the previous observations that most the particles are of sizes smaller than 20 μm, the effect of sieving the particles with a 20 μm opening size sieve is minimal. The bimodal particle size distribution pattern is more symmetrical than the previous ones, however, considering the observed variations in the particle size distribution, the observed symmetry may not be of consequence.

These results will be used as a baseline information level for the work to be performed in achieving a high capacity composite cathode capable of high discharge rate and excellent reversibility.

2.4 Charger

The preliminary charger development is in process. The version 0 charger hardware and software design was complete. The charger hardware is in fabrication. The version 0 charger is scheduled to complete on 12/31/94. Charger and pack electronics are designed to be used in the battery containing two cells in series. This electronics will be compatible with the SBD (Smart Battery Data) and SMBus (System Management Bus) standards being developed by Duracell and Intel.

CHAPTER 3.0

Exploratory R&D Technology on Rechargeable Batteries

3.1 Improved Solid Polymer Electrolyte

The objective of this task is to develop a solvent-free polymer electrolyte which provide sufficient conductivity and stability to be used in the high voltage rechargeable system. Unlike the gel-based polymer electrolyte which contains substantial amount of solvent/plasticizers, the solvent-free polymer electrolyte will provide interfacial stability to improve the cycle life. Our approaches are to investigate the co-polymer and single ion polymer, as shown in Figure 3-1.

Work was initiated on the synthesis of co-polymer. The preliminary experiment was conducted in the dry room. Methoxy polyethylene glycol monomethacrylate (PEM, Polysciences), 43.2 g was mixed with 19.8 g of polyethylene glycol dimethacrylate (PED) in a beaker. A 25 ml of 1M $LiAsF_6$/propylene carbonate was then added into the mix. A photoinitiator was then added. The mixed solution was UV radiated for various period of time. The film was drawn using the doctor blade. It was observed that the UV radiation generated significant heat resulting in inhomogeneous mix. The heating effect needs to be eliminated. The overcured mix could not be drawn and the undercured mix was too fluid to become free stand film. More experiment will be conducted in the next reporting period.

Initially, the single-ion polymer will focus on the synthesis of Li-SPEEK (Li salt to poly(acryl-ether-ether-ketone). This work will be conducted by Dr. Elizabeth Yen at JPL. The material will then be sent to ATK for characterization.

3.2 New SPE-Based Anode

This program also offers the opportunity to investigate various types of carbon and graphite materials for use as Li-ion electrodes. The ultimate objective is to integrate this Li-ion technology with the SPE cathodes.

We will trade off cycle life for improved energy density on the material selections based on the premise that moderate cycle life (500 cycles or better) is all that is needed in applications such as Thermal Weapon Sight (TWS) and notebook computer. For applications such as these, products with enhanced energy density in combination with moderate cycle life is more attractive than lower energy density batteries having cycle life capability in the thousands of cycles. This program, therefore, will look for those materials with high specific capacity mAh/g).

Initial effort will be to evaluate commercially available carbon/graphite materials in liquid-based electrolyte system. After final selection of candidate material, its integration with the SPE cathode systems will then be undertaken. Lonza's KS-44 graphite, with a reported capacity of 372 mAh/g, will be used to establish a baseline point. Meanwhile, we will attempt to develop a PPP-based[1] carbon, with a reported capacity of 680 mAh/g, to enhance the energy density of the "rocking chair" SPE system.

A thin film carbon anode was prepared using KYNAR (polyvinylidene fluoride) as a binder. A 3 % of KYNAR solution was prepared by dissolving 1 g of KYNAR into 30 g of methyl sulfoxide (DMSO). KS-44 graphite (Lonza) was then added into the solution and mixed well. A thin film was drawn on the stainless steel foil using doctor blade. Laboratory cells were built to anode capacity limit. Electrolyte solution was 1M $LiAsF_6$/ethylene carbonate/diethylene carbonate (EC/DEC). Cells are cycled at a 0.5 mA/cm^2 discharge rate and a 0.25 mA/cm_2 charge rate. A total of 36 cycles shown in Figure 3-2 has been accumulated to date. Typical discharge voltage profiles are presented in Figure 3-3. As can been seen, the initial capacity loss in the first discharge cycle is 15%. Cells have maintained 100% efficiency after the first cycle and testing of this cell is still ongoing.

---

1 Sato K., Noguchi M., Demachi A., Oki N., and Endo M., "A Mechanism of Lithium Storage in Disordered Carbons." Science, 264, 556 (1994).

APPROACH
SOLVENT-FREE SPE

A. Grafted Co-polymers

PEM (methoxy polyethylene glycol monomethacrylate)

\+

PED (polyethylene glycol dimethacrylate)

\+

Li salt

$\xrightarrow[\text{photoinitiator}]{\text{UV}}$ PEO-PMMA (polymethyl methacrylate)

- variables: Li Salts — $LiAsF_6$, $Li(CF_3SO_3)_2N$
  crown ether

B. Single-Ion Polymer

PEEK poly(aryl-ether-ether-ketone) ——> Li-SPEEK Li salt of PEEK

PEGME (polyethylene glycol methyl ether) ——> $CNP(EO)_n$ cyano ethylated PEGME

——> Acetonitrile ——> SPE

Figure 3-1. Approaches to Prepare the Solvent-Free Polymer Electrolyte

[S4773-1Q.wp]*paw

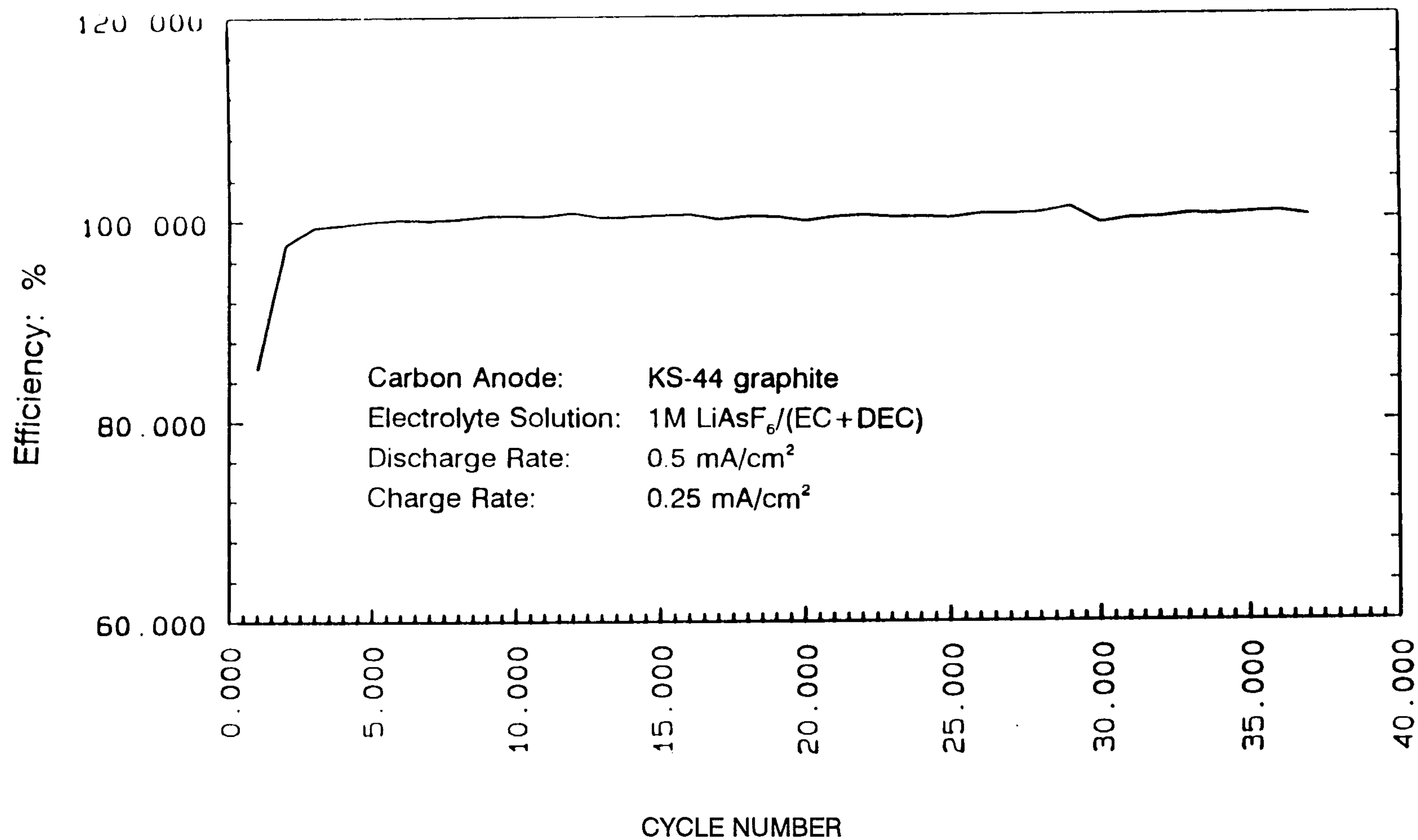


Figure 3-2. Li-ion/$LiCoO_2$ Cell Performance

[S4773-1Q.wp]*paw

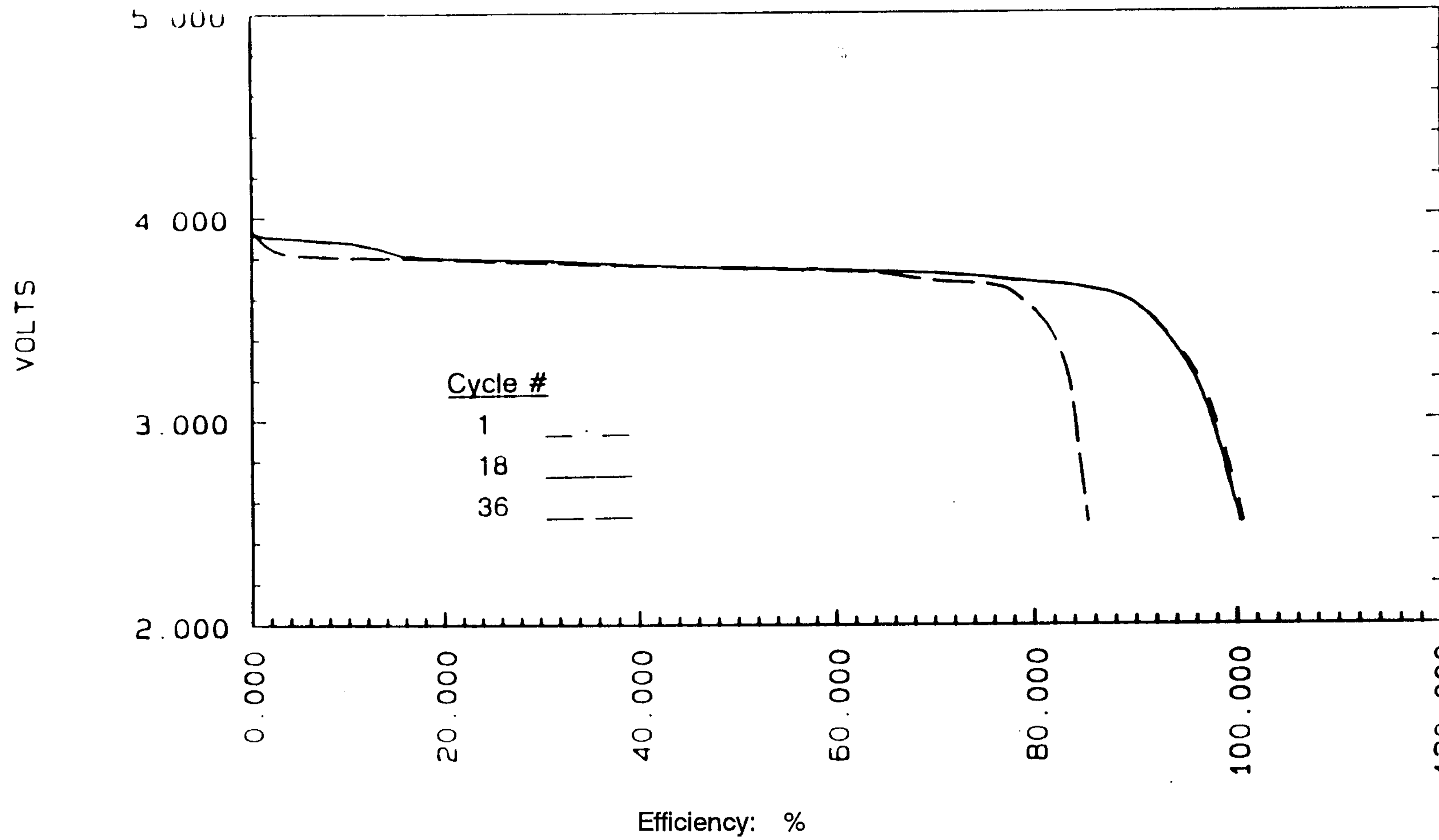


Figure 3-3. Discharge Voltage Profiles of Li-ion/$LiCoO_2$ Cells

CHAPTER 4.0

FUTURE WORK

Work to be conducted in the next quarter:

- Continue the development of a low resistance aluminum-based cathode current collector (ADL).
- Evaluate the polymer cells based on the aluminum current collector supplied by ADL.
- Continue the experiments of the synthesis of co-polymer and single-ion polymer.
- Continue the carbon anode work.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the experiments contributions of Mr. Kevin Burgess, Mr. Dave Hughes, Mr. Khiem Pham and Mr. Andrew Strobel, technical consultant of Dr. Venkatasetty and overall technical guidance of Dr. Dave Chua.

OFFICE OF THE UNDER SECRETARY OF DEFENSE (ACQUISITION)
DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22304-6145

IN REPLY REFER TO DTIC-OCC

SUBJECT: Distribution Statements on Technical Documents

TO: OFFICE OF NAVAL RESEARCH
CORPORATE PROGRAMS DIVISION
ONR 353
800 NORTH QUINCY STREET
ARLINGTON, VA 22217-5660

1995 1027 043

1. Reference: DoD Directive 5230.24, Distribution Statements on Technical Documents, 18 Mar 87.

2. The Defense Technical Information Center received the enclosed report (referenced below) which is not marked in accordance with the above reference.

QUARTERLY REPORT #1
N00014-94-C-0163
TITLE: FLEXIBLE MANUFACT.,
RAPID PROTOTYPING OF SOLID
POLYMER ELECTROLYTE (SPE),
RECHARGE. AMBIENT TEMP. BATT.

3. We request the appropriate distribution statement be assigned and the report returned to DTIC within 5 working days.

4. Approved distribution statements are listed on the reverse of this letter. If you have any questions regarding these statements, call DTIC's Cataloging Branch, (703) 274-6837.

FOR THE ADMINISTRATOR:

GOPALAKRISHNAN NAIR
Chief, Cataloging Branch

1 Encl

FL-171
Jul 93

DISTRIBUTION STATEMENT A:

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED

DISTRIBUTION STATEMENT B:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES ONLY; (Indicate Reason and Date Below). OTHER REQUESTS FOR THIS DOCUMENT SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT C:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES AND THEIR CONTRACTORS; (Indicate Reason and Date Below). OTHER REQUESTS FOR THIS DOCUMENT SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT D:

DISTRIBUTION AUTHORIZED TO DOD AND U.S. DOD CONTRACTORS ONLY; (Indicate Reason and Date Below). OTHER REQUESTS SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT E:

DISTRIBUTION AUTHORIZED TO DOD COMPONENTS ONLY; (Indicate Reason and Date Below). OTHER REQUESTS SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT F:

FURTHER DISSEMINATION ONLY AS DIRECTED BY (Indicate Controlling DoD Office and Date Below) or HIGHER DOD AUTHORITY.

DISTRIBUTION STATEMENT X:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES AND PRIVATE INDIVIDUALS OR ENTERPRISES ELIGIBLE TO OBTAIN EXPORT-CONTROLLED TECHNICAL DATA IN ACCORDANCE WITH DOD DIRECTIVE 5230.25, WITHHOLDING OF UNCLASSIFIED TECHNICAL DATA FROM PUBLIC DISCLOSURE, 6 Nov 1984 (Indicate date of determination). CONTROLLING DOD OFFICE IS (Indicate Controlling DoD Office).

The cited documents has been reviewed by competent authority and the following distribution statement is hereby authorized.

A

(Statement)

OFFICE OF NAVAL RESEARCH
CORPORATE PROGRAMS DIVISION
ONR 353
800 NORTH QUINCY STREET
ARLINGTON, VA 22217-5660

(Controlling DoD Office Name)

(Reason)

(Controlling DoD Office Address, City, State, Zip)

DEBRA T. HUGHES
DEPUTY DIRECTOR
CORPORATE PROGRAMS OFFICE

Debra Hughes

(Signature & Typed Name)

(Assigning Office)

19 SEP 1995

(Date Statement Assigned)